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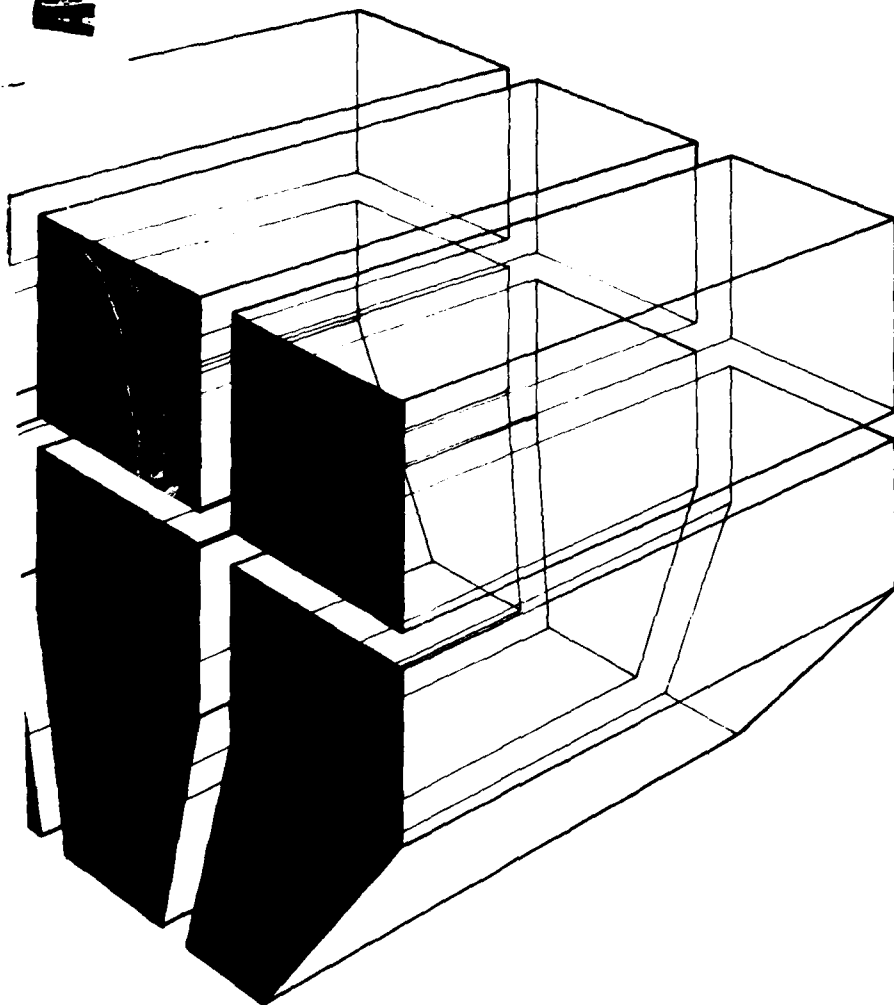
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INTERIM REPORT M-191
September 1976

Corrosion Effects on Construction Materials

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CHLORIDE SENSITIVITY OF THE CORROSION RATE
OF ZINC-COATED REINFORCING BARS



by
C. Hahn
S. Cato
W. Mattheessen

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This laboratory study was undertaken to determine whether zinc coatings can be relied on for long-term protection of reinforcing bars subject to environments of variable salt concentrations. Hot-dip galvanized reinforcing bars were coupled to bare carbon steel rebars in various concentrations of CaCl_2 in saturated $\text{Ca}(\text{OH})_2$ - distilled water solutions. Galvanic current output was monitored as a		

function of time and percent CaCl_2 for a zinc-steel couple with an anode-cathode area ratio of unity. Current output became stable after 20 days for CaCl_2 concentrations less than 1 percent. For concentrations at 1 percent or greater, current fluctuations were cyclical, increasing in magnitude as percent CaCl_2 increased. At 4 percent CaCl_2 , current output rose sharply.

FOREWORD

This research was conducted for the Directorate of Military Construction, Office of Chief of Engineers (OCE), under QCR 1.03.007, Project 4A762719AT41, "Design, Construction, and Operations and Maintenance Technology for Military Facilities," Task T7, "Materials Research and Development for Military Construction," Work Unit 002, "Corrosion Effects on Construction Materials." The work was performed by the Metallurgy Branch, Materials and Science Division of the U. S. Army Construction Engineering Research Laboratory (CERL).

OCE Technical Monitor for the work is Mr. C. Damico, DAEN-MCC-C.

Dr. A. Kumar is Chief of the Metallurgy Branch and Dr. G. Williamson is Chief of the Materials and Science Division. COL J. E. Hays is Commander and Director of CERL and Dr. L. R. Shaffer is Deputy Director.

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CHLORIDE SENSITIVITY OF THE CORROSION RATE OF ZINC-COATED REINFORCING BARS

1 INTRODUCTION

Problem Statement

Concrete, when placed in contact with metals, may be corrosive, neutral, or protective. The response of metal to concrete depends on the alloy composition, the constituents of the concrete, and the environment or service in which the concrete structure is placed. Many new procedures have been suggested for preventing the corrosion of steel in concrete; the suitability of these procedures for Corps of Engineers applications must be investigated.

Objective and Scope

This report documents part of a study to evaluate newly developed procedures for preventing corrosion of steel in concrete with respect to their suitability for inclusion in Corps of Engineers guide specifications.

The effectiveness of the procedures will be evaluated by several criteria. First, how much longevity can be expected and can any means be developed to predict this life? Second, does the procedure cause stress or deterioration of the concrete? Third, is the procedure economical and can it be expected to remain so for several years?

This interim report documents preliminary results of work on zinc-coated reinforcing bars exposed to alkaline and alkaline-chloride media. It considers only the first study criterion--longevity. Future study will complete the evaluation of longevity and address stress-deterioration and economic considerations.

Approach

The study phase reported here was accomplished as follows:

1. Literature was reviewed to place this experiment in the context of prior studies (Chapter 2).
2. Laboratory tests were performed on zinc-coated steel bars coupled to bare bars of equal length to determine the effect of chloride concentration on the corrosion rate of zinc (Chapter 3). The bars were submerged for 50 days in calcium chloride solutions of different concentrations, and corrosion rates were plotted as a function of time for each concentration.

2 BACKGROUND

This chapter reviews prior studies, describes the effects of concrete environments on steels, and discusses current thinking on the relationship between concrete cover and composition and its life span.

Response of Steel to Concrete

Portland cement in its dry state is composed of calcium oxide (CaO), silicon dioxide (SiO_2), and various other oxides. When water is added to concrete, the cement oxides form hydroxides and other cement mineral complexes which bind the aggregate. Water combines with CaO to form calcium hydroxide (Ca(OH)_2), the principal passivating agent in the concrete. The other constituents of concrete--sand, stone, and unground cement clinker--are essentially inert.¹ Uncombined water, which does not participate in the cement hydration and hardening reactions, acts as the solvent for carbonates, sulfates, and hydroxides in the concrete. This uncombined water solution may be a good or poor conductor, depending on which ions are dissolved in it and their concentrations.

The surface of a steel reinforcing bar reacts immediately with the alkaline concrete slurry to form ferrous hydroxide (Fe(OH)_2), which in turn reacts with dissolved oxygen to form $\gamma\text{-Fe}_2\text{O}_3$ or Fe_3O_4 . An imperfect oxide film halts corrosion of the steel, preventing further iron ions from going into solution. The oxide film remains intact as long as a uniform supply of hydroxyl ions and oxygen surrounds the entire surface of the bar.

The minimum pH required for passivation of steel in concrete has been reported² to be 11.5, although potential-pH (Pourbaix) diagrams have shown the minimum pH to be dependent on the potential of the steel.³ Since the pH of saturated Ca(OH)_2 is 12.5, the concrete in the vicinity of the bar remains basic as long as sufficient concentrations of hydroxyl ion are present. The pH is a direct measure of this hydroxyl ion concentration.

The passivation of a bare steel surface occurs quickly, as Hausmann⁴ demonstrated in both saturated Ca(OH)_2 and a Portland cement slurry (see Figure 1). As seen in Figure 1, the steel corrosion potentials of all

¹D. Lewis and W. Copenhagen, "Corrosion of Reinforcing Steel in Concrete in Marine Atmospheres," *Corrosion*, Vol 15 (1959), p 382.

²R. Shalon and M. Raphael, "Influence of Seawater on Corrosion Reinforcement," *Proceedings of the ACI*, Vol 55 (1958-9), p 1251.

³M. Pourbaix, "Application of Electrochemical Thermodynamics," *Lectures on Electrochemical Corrosion* (Plenum Publishing Corporation, 1973), p 19.

⁴D. Hausman, "Steel Corrosion in Concrete," *Materials Protection*, Vol 6, No. 11 (1967), p 19.

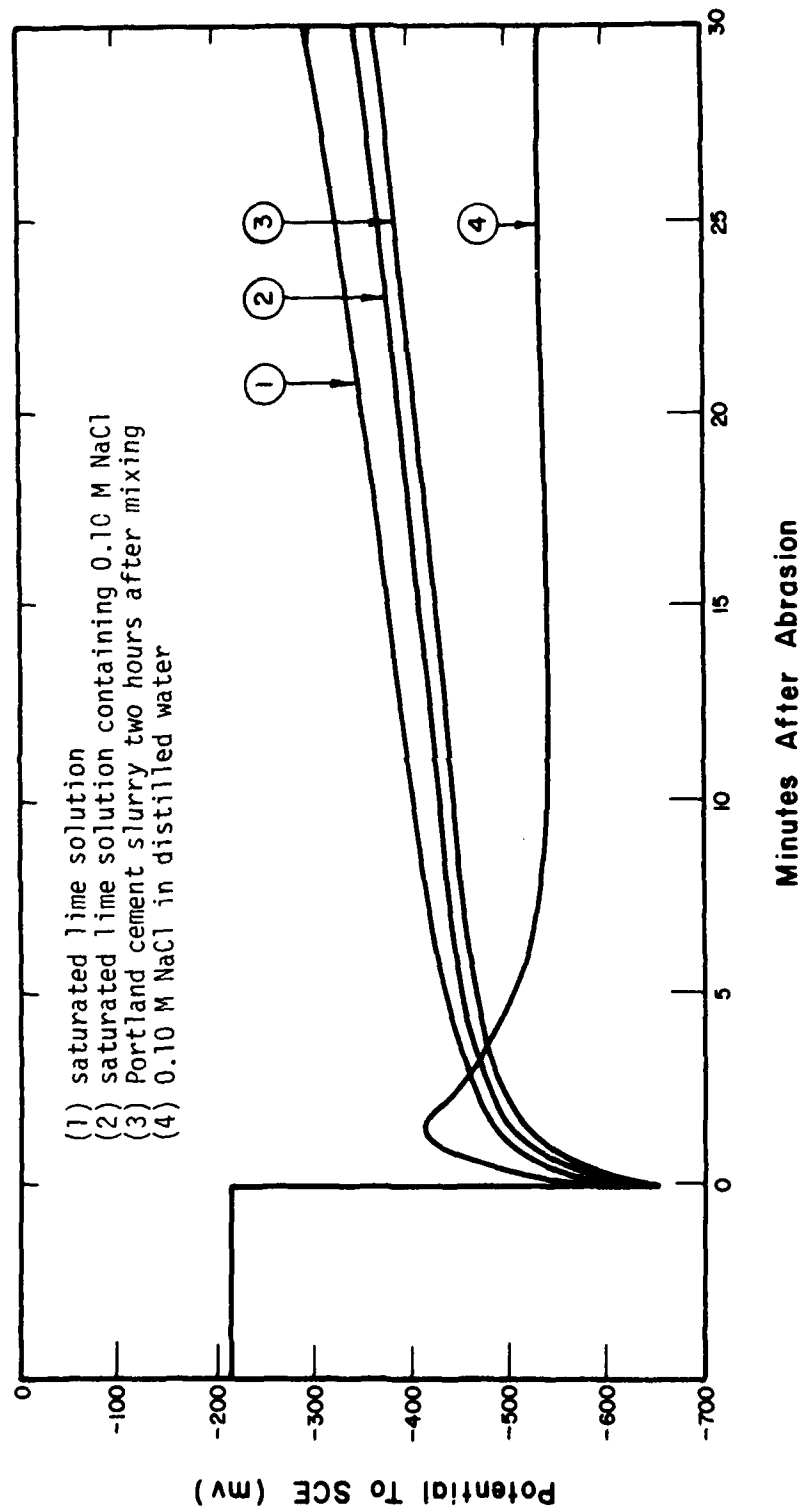


Figure 1. Potentials of steel wire in solution after surface abrasion. Reprinted with permission of the National Association of Corrosion Engineers from D. Hausman, "Steel Corrosion in Concrete," *Materials Protection*, Vol 6, No. 11 (1967), p 19.

the higher pH solutions became more positive (nobler) with time, whereas the neutral water solution (pH = 7) started to become passive but then rapidly broke down. Depassivation can also occur rapidly on a bare steel surface, which implies that the stability of protective films on steel is environment-sensitive.

Cracking of Concrete in Saline Solutions

Concrete is a heterogeneous solid composed of many particles which vary in size from microscopic to macroscopic dimensions. Some of the particles are engaged in bonding, some fill voids, and others are inert. Concrete has high concentrations of voids, many of which are interconnected. These voids may contain water filled with ions in solution, or they may be dry. Since concrete is not completely solid, there are many diffusion paths and capillary passageways where moisture can filter in and out.

Other structural inhomogeneities may develop in concrete, such as cracks resulting from shrinkage or loading, or the uneven distribution of aggregate particles because of poor mixing or pouring practices. These inhomogeneities cause permeability and capillarity to vary throughout the concrete. Variances in the properties of concrete can lead to formation of sites with high oxygen concentrations or low pH.

In fresh water with high resistivity ($> 10,000$ ohm-cm), ionic concentrations are insufficient to cause major changes in oxygen concentration. Unless the concrete cracks in spots and residual Ca(OH)_2 is washed away, the pH will remain > 11.5 . Although the initial driving potentials of differential aeration cells in low conductivity solutions are low (10 to 20 mV), they increase to substantial values after corrosion begins.⁵ The depth of cover is significant in damping out these variations in oxygen, dissolved solids, and pH. The wisdom of American Concrete Institute requirements⁶ for minimum concrete cover over reinforcing bars is evident in Figure 2, where a light concrete ($< 1/2$ in. [1.3 cm]) skin on a precast concrete panel shows excessive spalling and discoloration. This structure is not exposed to industrial pollution and sustains only moderate rainfall. Figure 3 is the underside of a rail trestle showing advanced deterioration where water seepage from above has passed through cinders and caused spalling.

⁵H. Uhlig, "The Oxygen Electrode and Differential Aeration Cell," *Corrosion and Corrosion Control* (John Wiley and Sons, Inc., 1971), pp 26-27.

⁶American Concrete Institute Standard 318-71, *Building Code Requirements for Reinforced Concrete* (American Concrete Institute, 1971), p 21.



Figure 2. Precast reinforced concrete panels exposed to rural atmosphere with 1/4 in. [0.6 cm] cover in the spall zones.



Figure 3a. Underlayment of trestle showing spalling of concrete and corrosion of steel supports.



Figure 3b. Deterioration of reinforced concrete beam of same rail trestle. Cover is about 1 to 1 1/2 in. [2.5 - 3.8 cm]. Note severe cracking of beam at mid-section on right.

Carbon dioxide can react with the Ca(OH)_2 to yield CaCO_3 , which also lowers pH.⁷ If cracking is induced by mechanical loading or thermal stresses, a seepage of slightly acidic water can also deplete the supply of hydroxyl ions.

However, if the concrete is in a more hostile environment, such as in a salt water estuary or acidic mine waters, the depletion of Ca(OH)_2 surrounding the steel can occur more rapidly. Chlorides are especially problematic because of their abundance in both fresh and salt waters. The wide use of deicing salts on highway pavements and bridges also represents a major source of concrete deterioration induced by rebar corrosion.

Adding ions like Cl^- to concrete increases the conductivity of the concrete and the ion concentrations may vary sharply since concrete is inhomogeneous. When the concrete is first exposed to a saline environment, the low Cl^- concentration in the concrete will gradually increase to that of the surrounding environment through uptake of the bulk fluid by capillarity and diffusion. However, several investigators^{8,9,10} found that after prolonged exposure, the concentrations were much greater than in the bulk solution. In the San Mateo bridge,¹¹ exposed for more than 30 years, concentrations were almost equal to saturated sodium chloride (NaCl) (26 percent) whereas the bay concentration is only about 4 percent salt.

Stratfull¹² has proposed that chloride accumulation proceeds by gradual bulk fluid absorption by capillarity, and that chloride concentration eventually occurs as the water of solution evaporates during the drying cycle. Stratfull also correlated the evaporable water content to water-cement ratio by an empirical equation:

$$E = k \frac{W^{1.2}}{C^{0.72}} + C_0$$

⁷A. Tripler and W. Boyd, "Corrosion of Reinforcing Bars in Concrete," *Proceedings of the 24th National Association of Corrosion Engineers Conference* (Houston, 1968), p 322.

⁸R. Stratfull, "Corrosion of Reinforced Concrete Bridge," *Corrosion*, Vol 13 (1957), p 173.

⁹J. Beaton, D. Spellman, and R. Stratfull, "Corrosion of Steel in Continuously Submerged Reinforced Concrete Piling," *Highway Research Board Record*, Vol 204 (1967), p 11.

¹⁰H. Finley, "Corrosion of Reinforcing Steel in Concrete Marine Atmospheres," *Corrosion*, Vol 17 (1961), p 104.

¹¹Finley, p 104.

¹²R. Stratfull, "How Chlorides Affect Concrete Used with Reinforcing Steel," *Materials Protection*, Vol 7 (1968), p 29.

where E = evaporable water content

W = percent water added to concrete mix

C = sacks of cement per cubic yard of concrete

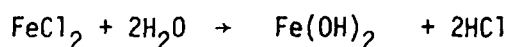
k, c₀ = empirical constants.

Stratfull found that concretes which were allowed to air-dry rather than fog- or steam-cure were highly absorbtive. High water-to-cement ratio concretes lost water quickly, which rendered them more susceptible to chloride intake.

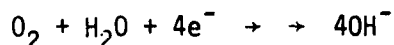
Other investigators, like Atimtay and Ferguson,¹³ have recommended a minimum water-to-cement ratio of 5.5 gal/sack. The more moisture the concrete contains as a result of curing, coupled with increased cement content, the better resistance to cracking.

Since even high quality concretes sustain cracks and take in chlorides, appreciable changes can occur in the vicinity of the rebar as varying concentrations of chloride build up. As chloride concentration increases, the solubility of oxygen decreases. This sets up cells where oxygen is excluded, and solvation of iron takes place more readily. The cause of this increased solvation tendency of iron in the presence of Cl⁻ has been the subject of much speculation. The most prominent theories are (1) competitive absorption of Cl⁻, (2) penetration of Cl⁻ through the passive layer, (3) formation of iron complexes, and (4) electrostatic attraction of Cl⁻ to iron.

However, the accumulation of Cl⁻ in a confined region such as a crevice or pit causes acidification through hydrolysis of an acid salt:¹⁴



The oxygen depletion of this confined area prevents the formation of ferric hydroxide or hydrated oxides, which can stifle further reaction of iron. These corrosion products precipitate some distance from the oxygen-depleted area in a region where more oxygen is available. The electrons generated by ionization of iron are consumed by the reaction:



which occurs at an adjacent non-acidic cathodic site. This series of events is the onset of chloride attack.

¹³E. Atimtay and P. Ferguson, "Early Chloride Corrosion of Reinforced Concrete," *Journal of American Concrete Institute*, Vol 70-9 (1973), p 606.

¹⁴M. Fontana and N. Greene, *Corrosion Engineering* (McGraw-Hill, 1967), p 43.

There is considerable disagreement as to what threshold level of Cl^- is responsible for premature failure of concrete. A Cl^- threshold of 700 ppm has been reported,¹⁵ although Newman¹⁶ and Blenkinsop¹⁷ noted that up to 2 percent CaCl_2 in concrete admixtures had no detrimental effect. Approximately half the CaCl_2 admixture becomes free Cl^- , according to Wohlhuter and Morris.¹⁸

As more and more of the corrosion products of iron are produced, the greater the space they occupy. Eventually, as the corrosion products occupy more space than the interface will permit, the concrete must expand. Since concrete is weak in tension, cracking and spalling will then occur. Cracking, in turn, permits more influx of the corrosive environment to leach out $\text{Ca}(\text{OH})_2$ and more easily release corrosion products. The thickness of the concrete cover also is related to this cracking, since thick covers can accommodate greater corrosion product pressures than thin covers. These failure mechanisms are diagrammed in Figure 4.

The Problem of Protective Coatings

Both metallic and nonmetallic coatings have been investigated¹⁹ as corrosion-preventive coverings for rebars. Of the metallic coatings, zinc has been most widely used because of its sacrificial nature and fairly low cost. Although zinc corrodes rapidly in highly acid ($\text{pH} < 3$) or highly alkaline ($\text{pH} > 13$) solutions,²⁰ it has a very low corrosion rate in the pH ranges of ordinary Portland cement concrete (11.5 to 13). Unless the cement contains potassium or sodium oxides, the pH should be no greater than 12.5--the pH of saturated $\text{Ca}(\text{OH})_2$. Zinc coatings on bars do not impair bonding properties, but are reported²¹ to be better or at least equal to the bond strength of bare steel to concrete.

¹⁵D. Hausman, "Steel Corrosion in Concrete," *Materials Protection*, Vol 6, No. 11 (1967), p 19.

¹⁶A. Newman, "Effects of Addition of CaCl_2 to Portland Cement Concrete," *Concrete and Construction Engineering*, Vol 38 (1943), p 159.

¹⁷J. Blenkinsop, "Effect on Normal 3/8 in. Reinforcement of Adding CaCl_2 to Dense and Porous Concretes," *Magazine of Concrete Research*, Vol 15-43 (1963), p 33.

¹⁸C. Wohlhuter and R. Morris, "Aspects of Steel Corrosion in Concrete," *Die Siviele Ingenieur in Suid-Afrika*, Vol 15-9 (1973), p 245.

¹⁹J. Clifton, A. Beeghly, and R. Mathey, *Nonmetallic Coatings for Concrete Reinforcing Bars*, Report PB 236-424 (Federal Highway Administration, February 1974).

²⁰B. Roetheli, G. Cox, and W. Littreal, "Effect of pH on the Corrosion Products and Corrosion Rate of Zn in Oxygenated Aqueous Solutions," *Metals and Alloys*, Vol 3 (1932), p 73.

²¹I. Cornet and B. Bresler, "Corrosion of Steel and Galvanized Steel in Concrete," *Materials Protection*, Vol 5, No. 4 (1966), p 69.

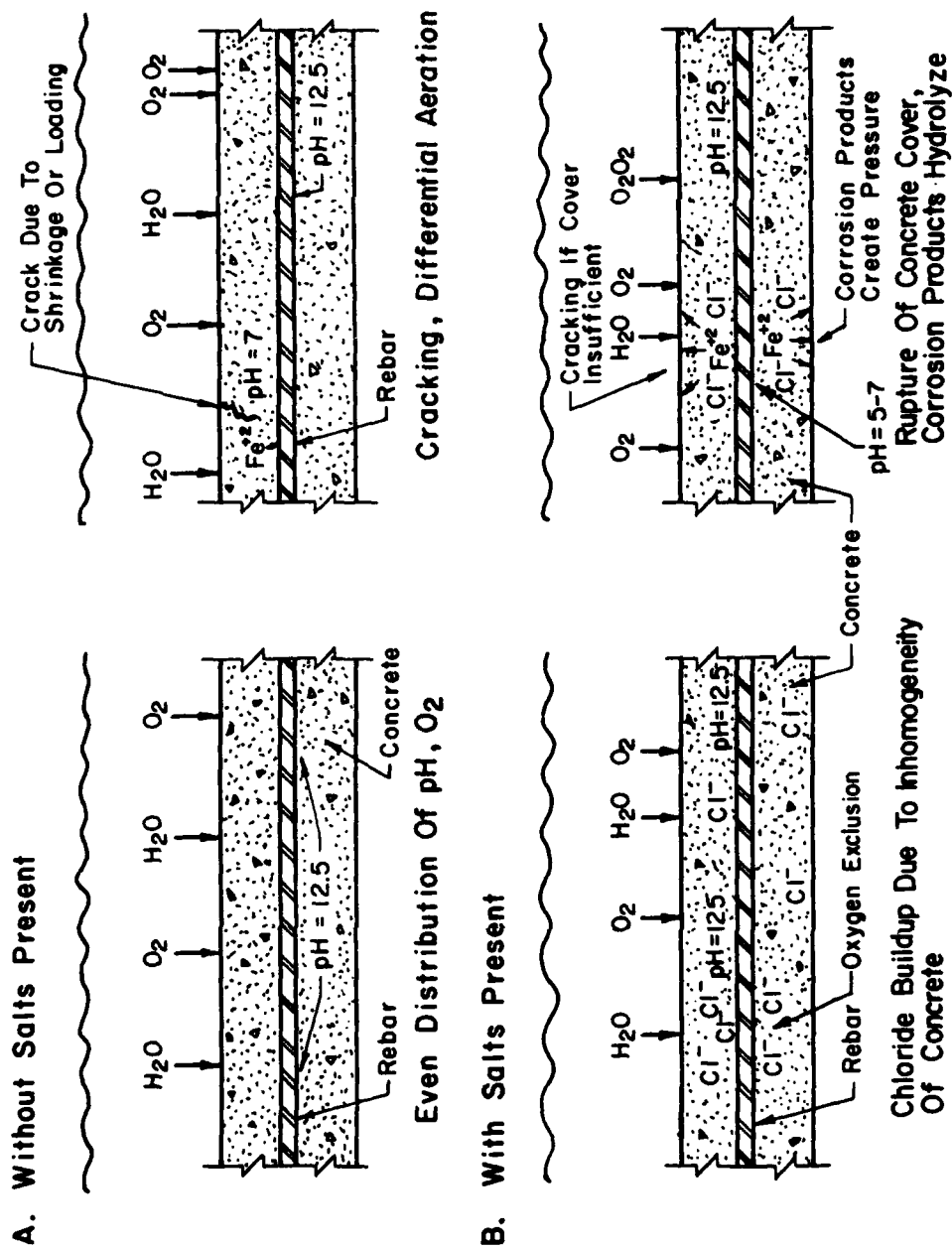


Figure 4. Failure mechanisms in concrete exposed to fresh and saline waters.

Tripler and Boyd²² reported in their potentiodynamic studies of zinc in 3.5 percent NaCl and saturated Ca(OH)₂, that the passivating reaction is the formation of Zn(OH)₂. Film breakdown occurs with the formation of ZnCl₂. Chlorides therefore accelerate the corrosion rate by rupturing a Zn(OH)₂ film which acts as a corrosion barrier. Hoxeng and Prutton²³ demonstrated that increasingly slight additions of Cl⁻ (10 to 50 ppm) to synthetic tap water solutions actively raised potentials of zinc by nearly 0.3V. Hubbard and Shanahan noted similar active shifts of zinc in aqueous solutions of increasing Cl⁻ content up to 100 ppm.²⁴ More active shifts meant increased corrosion rates with more Cl⁻ content in these studies, although they were not conducted in alkaline media. If reinforcing bar is to be protected by zinc for long periods of time, some measurement of the corrosion rate of zinc in varying concentrations of Cl⁻ is needed for prediction of rebar life.

Since prior work has not considered the deterioration of zinc in alkaline-chloride media, this study was intended to test zinc sensitivity in both saturated Ca(OH)₂ and actual concrete. Moreover, direct measurement of the kinetics of zinc consumption was sought instead of more conventional potential studies.

3 EXPERIMENTAL PROCEDURES

Testing Apparatus

Steel reinforcing bars (#4 deformed bars) were commercially hot-dip galvanized with Prime Western grade zinc. The average thickness of the zinc coating was determined by (1) cross-sectioning random portions of the rebar, (2) metallurgically polishing each section and etching with nitric acid and methyl alcohol, and (3) measuring the coating with a Zeiss optical microscope with a calibrated filar eyepiece. The average thickness was 0.152 mm; thickness variations are reported in Table 1.

Each bar was drilled on each cut end to accept a solid #12 gauge copper wire. After 0.8 in. (2 cm) of TW wire insulation was stripped away, the copper wires were soldered to the reinforcing bars on each end. The soldered joint was sealed with General Electric RTV silicone compound.

²²A. Tripler and W. Boyd, "Corrosion of Reinforcing Bars in Concrete," *Proceedings of the 24th National Association of Corrosion Engineers Conference* (Houston, 1968), p 322.

²³R. Hoxeng and C. Prutton, "Electrochemical Behavior of Zinc and Steel in Aqueous Media," *Corrosion*, Vol 5 (1949), p 330.

²⁴D. Hubbard and C. Shanahan, "Corrosion of Zinc and Steel in Dilute Aqueous Solutions," *British Corrosion Journal*, Vol 8 (November 1973), p 270.

Table 1
Average Thickness of Zinc Coating

<u>Sample Number</u>	<u>No. of Readings</u>	<u>Avg. Thickness, mm</u>
1	9	0.17
2	7	0.16
3	7	0.17
4	7	0.15
5	8	0.15
6	7	0.11

A banana plug was soldered to the end of each copper lead wire to obtain current and resistance measurements. Each galvanized reinforcing bar had a companion uncoated deformed bar of equal length and nominal diameter. All bars were 16 in. (40.6 cm) long and were weighed to the nearest 0.01 g.

The testing apparatus (Figure 5) consisted of a 50-liter polyethylene tank which provided an immersion bath for the bars. Bars were suspended in the tank by a notched, paraffin wax-impregnated wooden rack which kept the bars equidistant from each other. Two-in. (5.1 cm) centers were maintained to prevent variances in voltage drop from specimen to specimen. The wooden frames were suspended by stainless steel rods.

Each tank held a different concentration of CaCl_2 in a saturated solution of $\text{Ca}(\text{OH})_2$ dissolved in distilled water. One control solution contained only saturated $\text{Ca}(\text{OH})_2$. Each container held two couples (4 bars total) plus a galvanized uncoupled bar. All bars were fully immersed at all times.

Each coated bar was galvanically coupled to an uncoated bar via a junction box. When current flow was measured, a switching arrangement placed an ammeter directly in series with the bar without interrupting current flow (see Figure 6).

An uncoupled galvanized control bar was also placed in the suspension rack, with copper leads attached for potential and resistance measurements.

Test Procedures

The current output of every couple was read daily with a Keithley Model 164 Digital Multimeter, sensitive to ± 0.1 nA and having 0.2

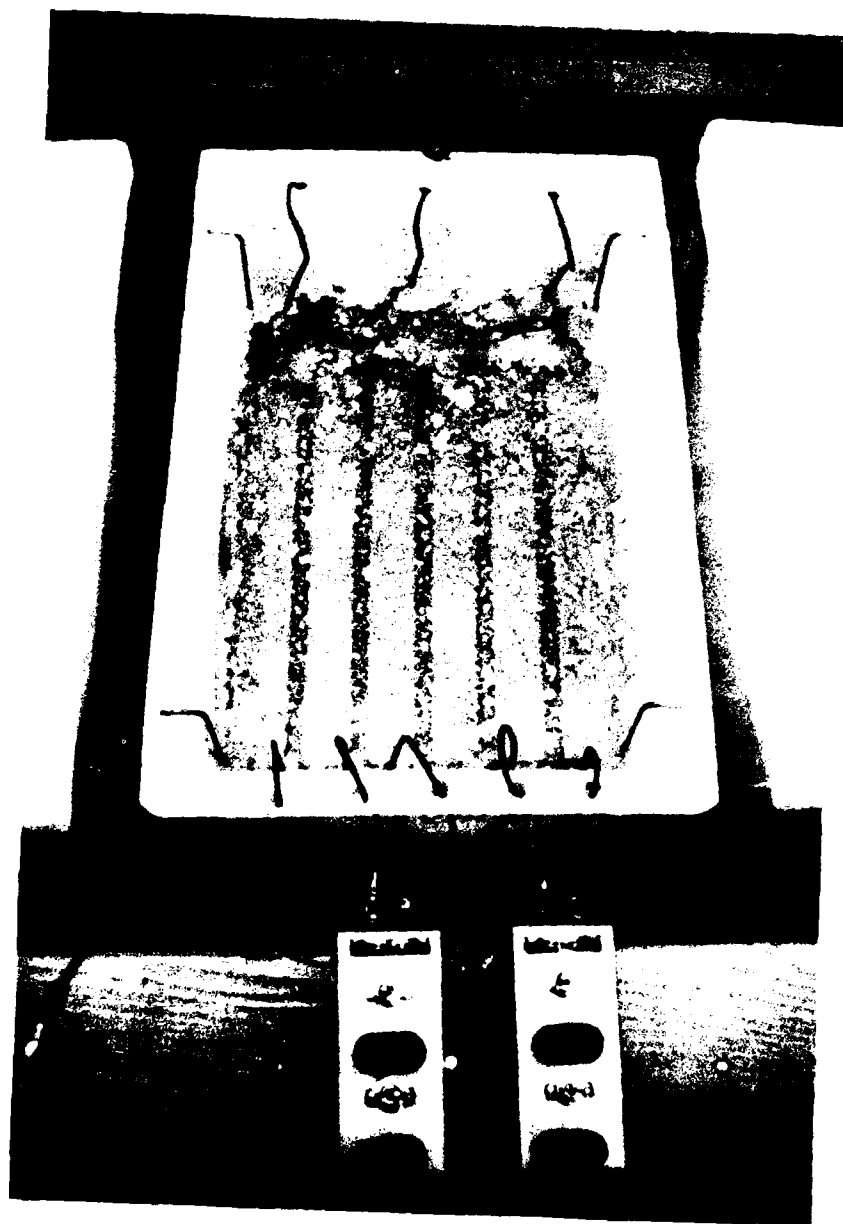
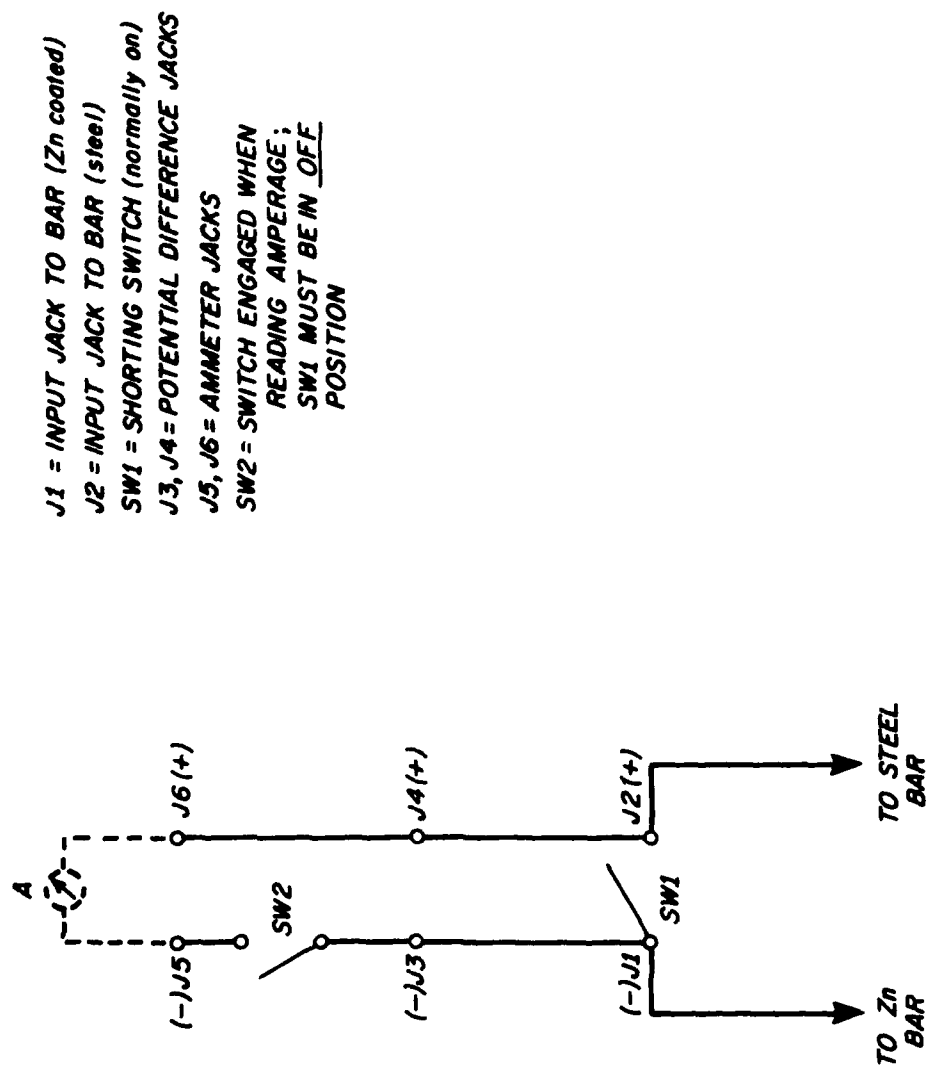


Figure 5. Test apparatus for measuring galvanic output of zinc-coated bars. Bars are uniformly 2 in. apart.



J1 = INPUT JACK TO BAR (Zn coated)
 J2 = INPUT JACK TO BAR (steel)
 SW1 = SHORTING SWITCH (normally on)
 J3, J4 = POTENTIAL DIFFERENCE JACKS
 J5, J6 = AMMETER JACKS
 SW2 = SWITCH ENGAGED WHEN
 READING AMPERAGE;
 SW1 MUST BE IN OFF
 POSITION

Figure 6. Ammeter junction box and shorting-switch.

percent accuracy in the milliamperage range. Changes in the resistance of each coated bar were also measured by this instrument weekly.

Temperature variations in the container were sensed by a capillary bulb of a Taylor Instrument thermograph. Average temperature was $68 \pm 3^\circ\text{F}$ ($293 \pm 2^\circ\text{K}$).

After each reading, the ammeter was removed from the circuit via the junction box without halting current flow, and the bar remained coupled until the next reading period. Times were noted to determine ampere-seconds (coulombs) for weight loss calculations.

Corrosion rates were calculated by the following equation:

$$\text{mpy} = \frac{129 \text{ iM}}{z\rho}$$

where mpy = corrosion rate in mils/yr ($0.0254 \text{ mm} = 1 \text{ mil}$)

i = corrosion current, mA/cm^2

z = number of electrons transferred

M = average gram-atomic weight

ρ = density.

Two couples were placed in a saturated $\text{Ca}(\text{OH})_2$ -distilled water solution along with one galvanized uncoupled bar. Similarly, bars were placed in solutions containing 0.01 percent, 0.1 percent, 1 percent, 2 percent, and 4 percent CaCl_2 in a saturated $\text{Ca}(\text{OH})_2$.

The resistivity of each solution was measured by a Yellow Springs Instrument Model 31 conductivity bridge.

4 RESULTS AND DISCUSSION

The measured galvanic current flow between the zinc-coated bar and the bare steel bar is plotted in Figures 7 through 12. The concentrations of CaCl_2 in the saturated $\text{Ca}(\text{OH})_2$ are also shown.

The bars in distilled water and $\text{Ca}(\text{OH})_2$ (see Figure 7) show a current vs. time-of-exposure curve that rapidly decays in the first few days. After the rapid decay, a relatively stable plateau develops due to buildup of $\text{Zn}(\text{OH})_2$. Corrosion products further accumulate, resulting in a slow decay to a fairly low corrosion rate.

The addition of 0.01 percent CaCl_2 does not significantly change the current output of the couple, which relatively parallels the decay of the chloride-free solution. Figure 8 shows this parallel trend.

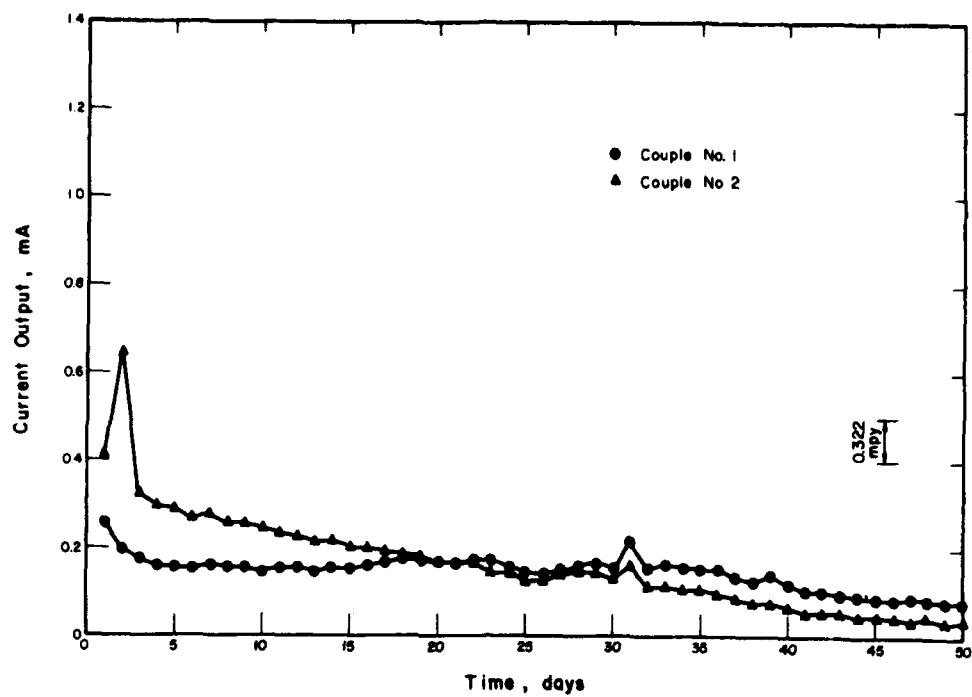


Figure 7. Galvanized rebar-steel rebar couple in 0 percent CaCl_2 .

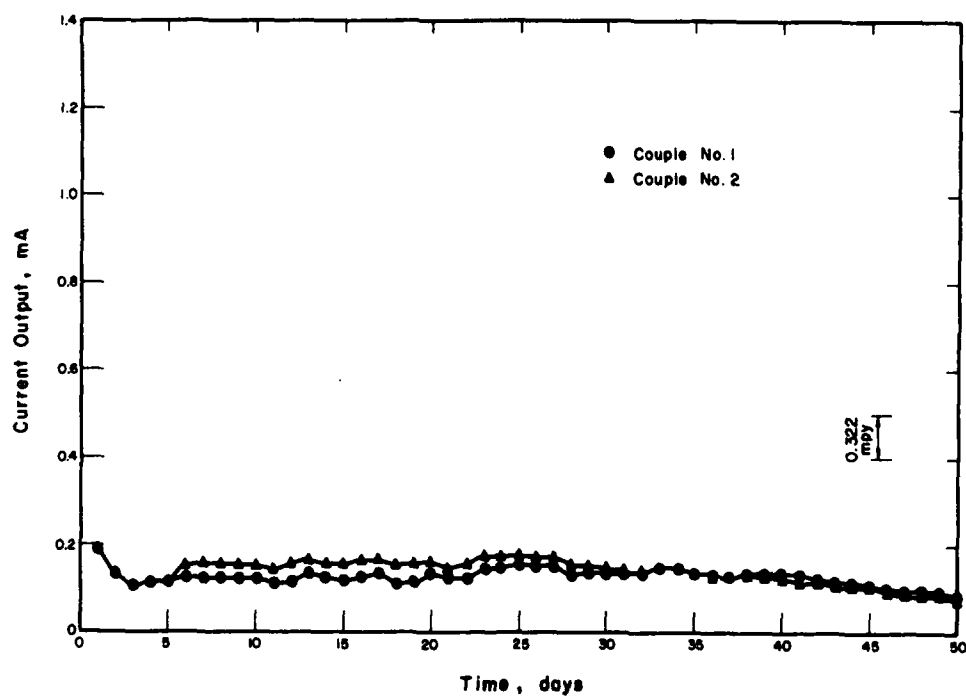


Figure 8. Galvanized rebar-steel rebar couple in 0.01 percent CaCl_2 .

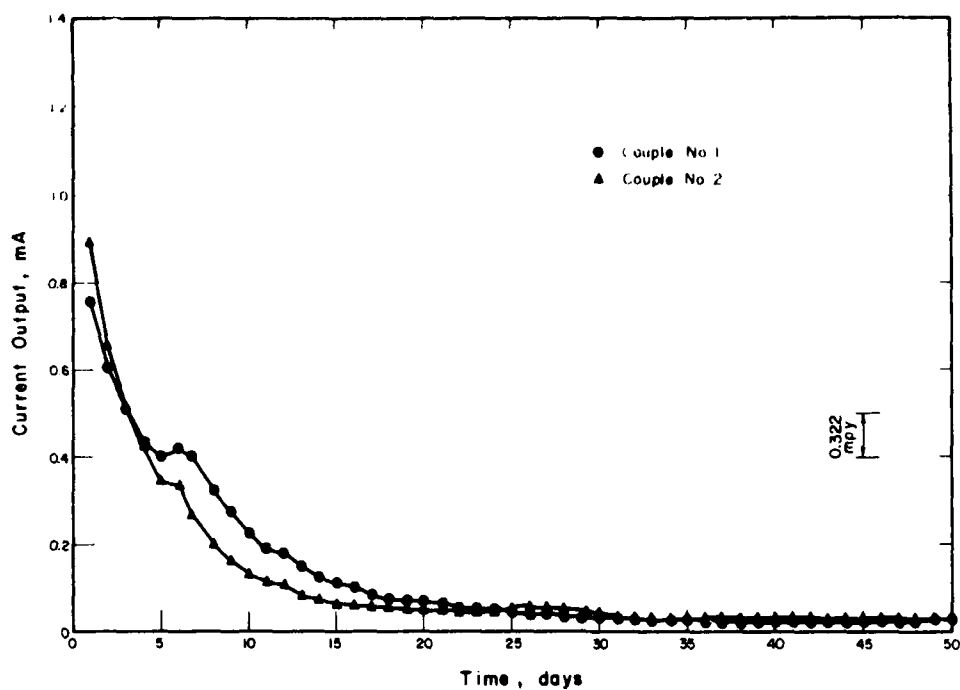


Figure 9. Galvanized rebar-steel couple in 0.1 percent CaCl_2 .

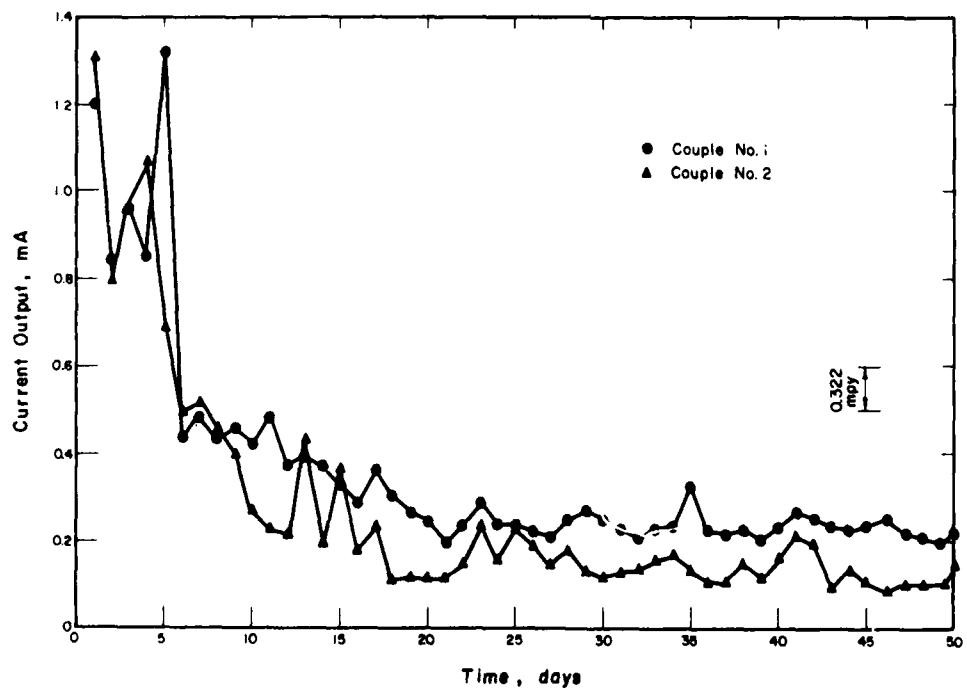


Figure 10. Galvanized rebar-steel rebar couple in 1.0 percent CaCl_2 .

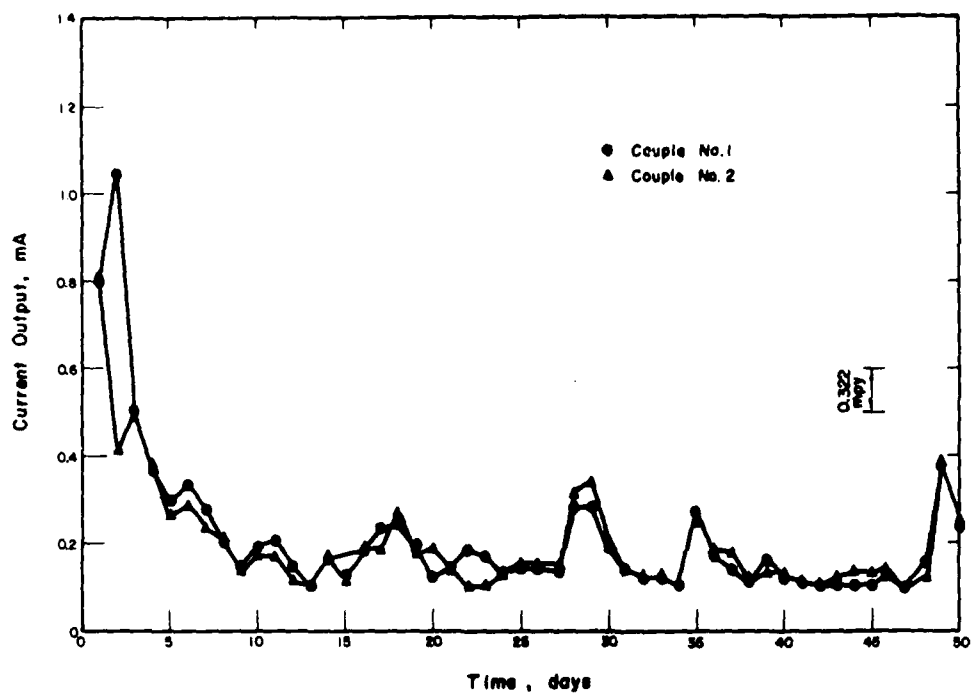


Figure 11. Galvanized rebar-steel couple in 2.0 percent CaCl_2 .

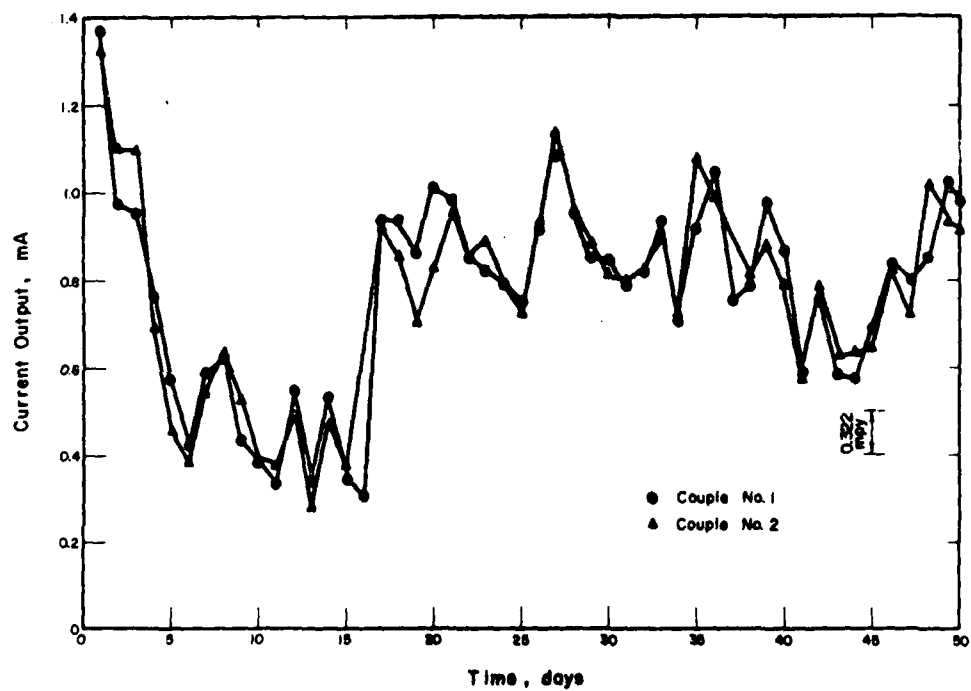


Figure 12. Galvanized rebar-steel rebar couple in 4.0 percent CaCl_2 .

Figure 9 reveals the same trend again at 0.1 percent CaCl_2 , with less fluctuation and difference in the output of each couple.

As the percent of CaCl_2 is increased to the 1.0 percent level, the plateau region seen in lower chloride solutions after the initial decay disappears. The current output is cyclic, with peaks of activity occurring every 8 to 10 days, then exponentially decaying. As shown in Figures 11 and 12, increases in CaCl_2 result in greater swings in current output difference between peak and valley. Each peak represents a breakdown in the Zn(OH)_2 passive film by ZnCl_2 and each valley represents the buildup of Zn(OH)_2 .

Figure 13 shows current output as a function of CaCl_2 concentration. For the first 10 days the corrosion rate rises linearly with log time. After 10 days, the corrosion rate is no longer linear but begins to jump exponentially at 4 percent CaCl_2 .

The method of measuring current output of galvanic couples with a 1:1 cathode-to-anode area ratio can be used to correlate corrosion rates of other anode-to-cathode area ratios. This can be accomplished since the area ratio is proportional to corrosion rate, as shown by Tripler

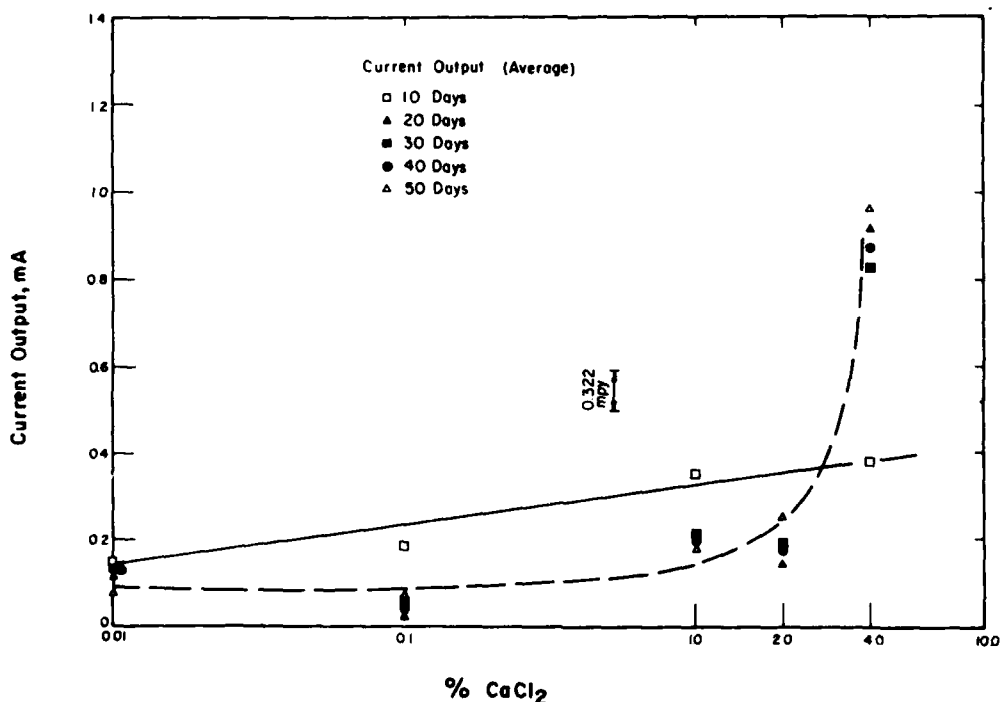


Figure 13. Galvanic current output of zinc-to-steel couples as a function of CaCl_2 concentration in saturated Ca(OH)_2 -distilled water solution.

and Boyd.²⁵ The self-corrosion rate can be determined by solving the "catchment" equation:

$$p = P_0 (1 + A_c/A_a)$$

where p = new penetration after coupling

P_0 = uncoupled penetration

A_c = area of cathode

A_a = area of anode.

However, the tests reported here are relative indications, and may not correspond exactly to zinc-dipped reinforcing bars of advanced age. Older bars would have similar anode-to-cathode area ratios, but current output might differ due to penetrations into the various phases of the zinc-iron binary solution.

Another problem is that the corrosion rates determined here may be applicable only to highly porous or ruptured-cover concretes, in which corrosion products are permitted to expand freely. The corrosion products of zinc may self-limit its own consumption in concrete, because the concrete may not permit further expansion. This factor was not evaluated in this study, since corrosion products formed freely and were not confined by concrete. Corrosion products tended to form in the valleys of the diamond-pattern of the reinforcing bar, and were somewhat knobby in shape and discontinuous in their distribution.

Resistance changes were found to be negligible.

5 CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. The galvanic corrosion rate of zinc in saturated Ca(OH)_2 was sensitive to the chloride concentration, and tended to rise perceptibly at ≥ 1 percent CaCl_2 , with an exponential rise at 4 percent CaCl_2 .
2. A discontinuous distribution of corrosion products may result in localized stresses if zinc-coated bars are imbedded in concrete exposed to high-chloride environments. However, the nature of these corrosion product forces and their growth in concrete-cover confinements is not known since this investigation permitted free expansion.

²⁵A. Tripler and W. Boyd, "Corrosion of Reinforcing Bars in Concrete," *Proceedings of the 24th National Association of Corrosion Engineers Conference* (Houston, 1968), p 322.

3. The proportionality of anode-to-cathode area ratio to corrosion rate for ratios <1 was not evaluated in this study, although the Tripler and Boyd²⁶ work established a basis to use this galvanic couple to determine actual corrosion rates by extrapolation. This study indicates that zinc-coated bars coupled to bare bars of equal length would sustain the same sensitivity to chlorides.

Recommendations

1. The corrosion rate of zinc concentrations >1 percent CaCl_2 in actual concrete should be evaluated to establish correlation with this laboratory simulation. This should be accomplished using actual bars with known cover-to-bar diameter and water-cement ratios. The proportionality of anode-to-cathode ratio to corrosion rate should also be analyzed for the possibility of using test couples throughout the concrete for predicting corrosion rates of fully coated bars.

2. The measurement of voltage in proportion to current should be evaluated over a longer period of time.

3. The nature of the stresses generated by the corrosion products of iron and zinc should be evaluated in-situ. Theoretical computations of expansion due to formation of iron oxide-hydroxides or chlorides cannot accurately predict stresses, since corrosion-product confinement is related to permeability and the strength of the concrete-metal interface.

4. Quicker and more accurate methods of determining chloride content profiles as a function of depth in concrete require further development for better prediction of corrosion rate.

5. Because the corrosion rate of zinc in concrete is chloride-sensitive, a Corps-wide adoption of zinc-coated bars cannot be recommended at this time. When accurate means of measuring the in-situ corrosion rate are completed, incorporation of zinc-coated rebars into existing guide specifications can then be considered.

6. A cost-benefit ratio analysis of the merits of zinc-coated bars compared to bare bars must also be completed prior to Corps acceptance.

²⁶A. Tripler and W. Boyd, "Corrosion of Reinforcing Bars in Concrete," *Proceedings of the 24th National Association of Corrosion Engineers Conference* (Houston, 1968), p 322.

REFERENCES

- American Concrete Institute Standard 318-71, *Building Code Requirements for Reinforced Concrete* (American Concrete Institute, 1971), p 21.
- Atimtay, E. and P. Ferguson, "Early Chloride Corrosion of Reinforced Concrete," *Journal of American Concrete Institute*, Vol 70-9 (1973), p 606.
- Beaton, J., D. Spellman, and R. Stratfull, "Corrosion of Steel in Continuously Submerged Reinforced Concrete Piling," *Highway Research Board Record*, Vol 204 (1967), p 11.
- Blenkinsop, J., "Effect on Normal 3/8 in. Reinforcement of Adding CaCl_2 to Dense and Porous Concretes," *Magazine of Concrete Research*, Vol 15-43 (1963), p 33.
- Clifton, J., A. Beeghly, and R. Mathey, *Nonmetallic Coatings for Concrete Reinforcing Bars*, Report PB 236-424 (Federal Highway Administration, February 1974).
- Cornet, I. and B. Bresler, "Corrosion of Steel and Galvanized Steel in Concrete," *Materials Protection*, Vol 5, No. 4 (1966), p 69.
- Finley, H., "Corrosion of Reinforcing Steel in Concrete Marine Atmospheres," *Corrosion*, Vol 17 (1961), p 104.
- Fontana, M. and N. Greene, *Corrosion Engineering* (McGraw-Hill, 1967), p 43.
- Hausman, D., "Steel Corrosion in Concrete," *Materials Protection*, Vol 6, No. 11 (1967), p 19.
- Hoxeng, R. and C. Prutton, "Electrochemical Behavior of Zinc and Steel in Aqueous Media," *Corrosion*, Vol 5 (1949), p 330.
- Hubbard, D. and C. Shanahan, "Corrosion of Zinc and Steel in Dilute Aqueous Solutions," *British Corrosion Journal*, Vol 8 (November, 1973), p 270.
- Lewis, D. and W. Copenhagen, "Corrosion of Reinforcing Steel in Concrete in Marine Atmospheres," *Corrosion*, Vol 15 (1959), p 382.
- Newman, A., "Effects of Addition of CaCl_2 to Portland Cement Concrete," *Concrete and Construction Engineering*, Vol 38 (1943), p 159.
- Pourbaix, M., "Application of Electrochemical Thermodynamics," *Lectures on Electrochemical Corrosion* (Plenum Publishing Corporation, 1973), p 19.

REFERENCES (cont'd)

- Roetheli, B., G. Cox, and W. Littreal, "Effects of pH on the Corrosion Products and Corrosion Rate of Zn in Oxygenated Aqueous Solutions," *Metals and Alloys*, Vol 3 (1932), p 73.
- Shalon, R. and M. Raphael, "Influence of Seawater on Corrosion Reinforcement," *Proceedings of the ACI*, Vol 55 (1958-9), p 1251.
- Stratfull, R., "Corrosion of Reinforced Concrete Bridge," *Corrosion*, Vol 13 (1957), p 173.
- Stratfull, R., "How Chlorides Affect Concrete Used with Reinforcing Steel," *Materials Protection*, Vol 7 (1968), p 29.
- Tripler, A. and W. Boyd, "Corrosion of Reinforcing Bars in Concrete," *Proceedings of the 24th National Association of Corrosion Engineers Conference* (Houston, 1968), p 322.
- Uhlig, H., "The Oxygen Electrode and Differential Aeration Cell," *Corrosion and Corrosion Control* (John Wiley and Sons, Inc., 1971), pp 26-27.
- Wohlhuter, C. and R. Morris, "Aspects of Steel Corrosion in Concrete," *Die Siviele Ingenieur in Suid-Afrika*, Vol 15-9 (1973), p 245.

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